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Chemical Physics Letters 404 (2005) 19–24
CHEMICAL PHYSICS LETTERS
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Temperature programmed desorption and infrared spectroscopic studies of thin water films on MgO(1 0 0)

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Received 3 December 2004

Abstract

Thin water (D_2O) films on MgO(1 0 0) surfaces have been studied. Water was deposited at 115 K and monolayer and multilayer films were prepared by annealing above 150 K, where the transition from amorphous solid to cubic ice is known to take place, and then re-cooling. Temperature programmed desorption traces and transmission Fourier transform infrared spectra were recorded. For the monolayer, results are consistent with an essentially flat, hydrogen-bonded water network without a significant amount of dangling OD. Ice growing on the monolayer appears to be a blend of amorphous and crystalline solid at 115 K, becoming more crystalline when annealed.

1. Introduction

Physical and chemical processes that transpire on metal oxide surfaces are, in general, influenced by defects, corrugation, and temperature [1]. Strongly bound monolayers are of particular interest because they are ubiquitous in nature, and they can act in concert with the native surface to provide environments that may either promote or hinder chemical change. Properties such as adsorbate orientation and binding energy are central to the roles played by the adsorbed monolayer.

Water is an adsorbate of paramount importance. Specifically, issues such as physisorption versus chemisorption and the orientation of water molecules in the first few monolayers deserve scrutiny, especially for metal oxides. These are generally less reactive than metals, though not necessarily at low coordination sites, which are known to play a role in catalysis [2]. In the case of metal oxide surfaces, terraces are typically less reactive than step edges, vacancies, and corners (hereafter referred to as 'defects').

Interactions of water on MgO(1 0 0) surfaces have attracted extensive experimental and theoretical efforts, and serve as useful prototypes. Among the questions of interest are: (i) Does water adsorb molecularly on terraces? (ii) What happens at defect sites? (iii) If water adsorbs molecularly, do the molecules hydrogen bond to form a reasonably flat monolayer, or do dangling OH bonds make a corrugated layer? (iv) How does the surface affect adsorption for overlayers? (v) Does the absorption mechanism vary with temperature? The goal of the present work is to further our understanding of interactions between MgO(1 0 0) and water by exploring interactions in coverage ranging from monolayers to thin films.

Theoretical calculations that use a broad range of methods, as well as numerous experiments, have been reported for the water/MgO(1 0 0) system [3–21]. Many of the computational studies find that at low temperatures water adsorbs molecularly on terrace sites, with a binding energy of ~0.8 eV for the first layer. Surface defects may or may not dissociate water to form hydroxyl groups; this remains an open question. In addition, if

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0009-2614/$ - see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.cplett.2005.01.049

dissociation at defect sites occurs, it is not known if the hydroxyl groups thus formed migrate onto the terrace. This can amplify the effect of site-induced dissociation. It is clear, however, that water interacts more strongly with low coordination defect sites than with terrace sites, whether dissociatively or molecularly.

The manner in which a MgO(100) surface is prepared affects the concentration of low coordination sites [2]. Surfaces of polished/annealed and sputtered/annealed metal oxides on average are less stoichiometric than cleaved surfaces. Air-cleaved MgO appears to be affected by water vapor, though this can be lessened considerably by cleaving in a dry nitrogen atmosphere or in ultrahigh vacuum and annealing in oxygen at low pressures. Step defects, however, are unavoidable on cleaved surfaces [2].

Because the surface preparation method affects results, it has been difficult to make meaningful comparisons between results obtained by different investigators, as well as to compare experiments to calculations. The experiments reported herein were carried out on crystals that were prepared in a way that is known to produce terraces of significant area and minimize oxygen vacancies [2].

The experiments were carried out by using transmission Fourier transform infrared (FTIR) spectroscopy and temperature programmed desorption (TPD) to characterize thin water films, ranging from sub-monolayer to multilayers, on MgO(100) surfaces that have been prepared by cleaving in dry nitrogen and removing oxygen vacancies. The geometry of water adsorbed on MgO(100) has been the subject of debate [3–21]. In recent experiments, Xu and Goodman [14] used reflection FTIR and TPD to study water adsorbed on MgO(100) grown on molybdenum, but were unable to study both *s* and *p* polarizations due to the surface selection rules. They concluded that the monolayer must be flat because the *p*-polarized signal was small. Heidberg et al. [15] studied transmission FTIR of water adsorbed on vacuum cleaved MgO, though coverage was not calibrated. They concluded that the monolayer was ordered and relatively flat. Several sharp peaks in *p*-polarization were attributed to step sites. However, the temperatures at which they observed different coverages calls to question the suggested coverages. The extent of dissociative desorption and its dependence on surface structure, temperature, and defect concentration are also subjects of current debate [13,22].

The TPD and FTIR measurements are complementary. TPD experiments provide information on the heats of adsorption of water monolayer and overlayers. They also enable calibration of coverage. Previous TPD studies have been carried out with MgO(100) surfaces prepared by sputtering and annealing [16]; epitaxial growth on molybdenum [14]; and polishing [17]. To the best of our knowledge, no TPD study of water on MgO(100) prepared by cleaving has been reported.

2. Experimental

The FTIR and TPD experiments were carried out in an ultrahigh vacuum (UHV) chamber whose base pressure is 1×10^{-10} Torr. The arrangement is shown in Fig. 1. MgO crystals (Marketech) are cleaved on each side in a dry nitrogen atmosphere, exposing (100) surfaces, and inserted immediately into the vacuum chamber. Crystal dimensions are typically 1 cm × 1 cm × 1 mm. After putting the sample in the chamber and achieving the base pressure by thorough baking, the surface was cleaned and oxygen vacancies were removed by heating in oxygen [1]. This yielded well-ordered, contaminant-free surfaces [1].

The surface holder consists of thin tantalum foil clips attached to tantalum wires and to tantalum rods fixed to copper blocks. The copper blocks are separated from the manipulator by a sapphire disk for electrical isolation, allowing the crystal to be heated resistively. A precision manipulator (Kurt J. Lesker, essential modifications by McAllister Technical Services) is capable of *XYZ* translation as well as 360° rotation. It has a hollow stainless steel tube with a copper block at the end, to which the surface holder is attached. Cooling is achieved by filling the tube with liquid nitrogen, and the surface temperature is measured by using a *k*-type thermocouple attached to the crystal face with ceramic glue. With this configuration, the surface routinely cools to 115 K, which is low enough for the system under consideration here.

The FTIR studies were carried out with a Nicolet Protegé 460 spectrometer with a liquid nitrogen cooled

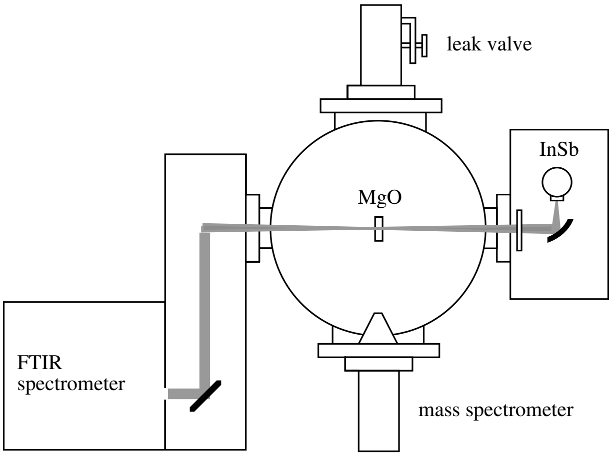

Fig. 1. Schematic of experimental arrangement. IR radiation is reflected from a flat mirror and a focusing mirror (150 mm focal length) before entering the UHV chamber through a CaF_2 window. It passes through the rotatable MgO(100) crystal with a diameter of ~8 mm and exits the chamber through a CaF_2 window. It passes through a wire grid polarizer and is focused (45 mm focal length) onto a 2 mm diameter InSb detector element. The path is purged to remove atmospheric water and carbon dioxide. A precision leak valve doses water and a residual gas analyzer with a narrow aperture observes molecules desorbed from the surface in TPD studies.

InSb detector. The IR beam is focused into the UHV chamber by using a system of mirrors (Fig. 1). It passes through CaF_2 windows and the MgO crystal, and is focused onto the detector. The IR source bench, mirrors, and detector are purged of atmospheric water and carbon dioxide by using a Whatman purge gas generator. A wire grid polarizer (Molectron, BaF_2 substrate, finely spaced aluminum wires, 93–98% polarization purity), is placed in the beam path, and the crystal is oriented at 50° from the normal for the polarization studies. The FTIR spectra average 500–1500 scans at 2 cm^{-1} resolution. During data acquisition, spectra with severely sloping baselines are stopped and the surface is heated to remove adsorbed water before repeating the experiment.

A residual gas analyzer (Stanford Research Systems, RGA300) is attached to the chamber perpendicular to the IR beam path. It is used to monitor desorbed water in the TPD experiments. D_2O (Aldrich 99.9%) is degassed by several freeze–pump–thaw cycles before being introduced into the chamber by using a precision leak valve (MDC). The system is passivated with D_2O to reduce the amount of H_2O and HDO in the chamber. This is checked periodically by monitoring isotopic ratios during desorption.

3. Results

The TPD experiments were carried out by heating the surface at a rate of ~2 K/s and monitoring mass 20 (D_2O^+) with the mass spectrometer. Care was taken to prevent electrons generated by the ion source of the mass spectrometer from reaching the surface, as these electrons are known to wreak havoc with adsorbates [23]. When this precaution was not heeded, additional features were observed that are unrelated to water desorption. Fig. 2 shows TPD spectra obtained by using nitrogen-cleaved MgO. These spectra are similar to those obtained in previous studies, in that they clearly show peaks that are assigned to a monolayer ($T_p = 240$ K) and to multi-layers ($T_p = 165$ K). The monolayer peak is broad, but appears at temperatures that are in reasonable agreement with the previously determined heat of desorption of water (~0.8 eV). Namely, Redhead analysis (with $T_p = 240$ K and $\nu \sim 10^{15}\ s^{-1}$) yields 0.75 eV. The TPD spectra allow the amount of water adsorbed on the surface to be determined accurately. Moreover, the large temperature separation between monolayer and over-layer features enables monolayer coverage to be achieved by dosing in the multilayer regime and then desorbing over-layers, leaving just the annealed monolayer.

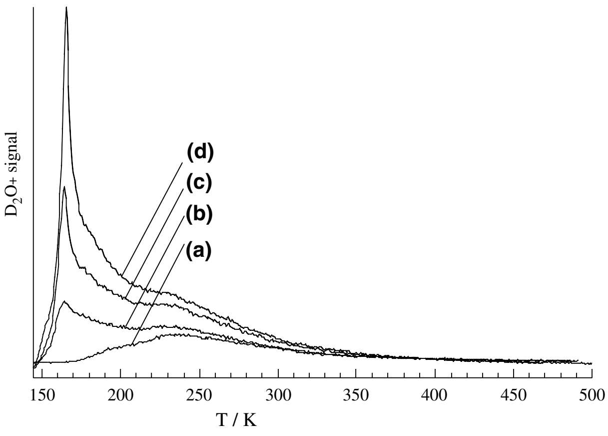

Fig. 2. TPD of D_2O on MgO(1 0 0). Coverage increases from a monolayer (a) to ~five layers (d).

Dosing the 115 K surface with water yields a solid that is mainly amorphous. It is converted to cubic ice by annealing above 150 K. This well-known transition [24–26] is illustrated in Fig. 3, which shows spectra recorded in the ν_1/ν_3 (i.e., OD stretch) region for D_2O that has been adsorbed on MgO(1 0 0) both before and after annealing past the transition temperature. Spectra recorded with *s* and *p* polarizations show the distinctive peak shapes of crystalline ice after annealing for a coverage of ~15 layers (Fig. 3c and d).

Though cubic ice features are present in FTIR spectra recorded prior to annealing (see Fig. 3a and b), they are enhanced by annealing above 150 K. Also apparent in unannealed samples is a small *p*-polarized peak at 2727 cm^{-1} that we believe is due to 'dangling' OD bonds. Higher doses of water (50–150 layers) show no deviation from the aforementioned observations. Though the signature of the OD dangling bond is observed with even smaller thicknesses of unannealed solid, it is not seen in spectra that have been recorded with monolayer coverage, which are nearly always obtained after annealing. The 2727 cm^{-1} peak reaches its maximum intensity at ~5 layers. Thereafter its intensity does not increase. Annealed ice has a cubic structure that eliminates dangling bonds. Also, spectra of cubic ice are similar in *s* and *p* polarizations, while differences in shape between *s* and *p* polarizations are evident in the corresponding spectra taken without annealing.

Annealed ice begins to lose its characteristic peak structure when the coverage is below ~10 layers. Nonetheless, the ν_1/ν_3 absorption feature remains broad and featureless down to sub-monolayer coverage. Fig. 4 shows unpolarized spectra in the D_2O stretch region for coverages of 1, 3, and 5 layers. The peak remains broad and red shifted relative to the gas phase values of 2671 and 2788 cm^{-1}, for ν_1 and ν_3, respectively [27]. Polarized spectra of the monolayer display line shapes that are similar to those observed in the unpolarized spectra (Fig. 4), albeit with low S/N. Though broad line widths and low S/N make it difficult to determine peak areas for monolayer coverage, *s* polarization is favored slightly in all cases. The low S/N cannot be improved

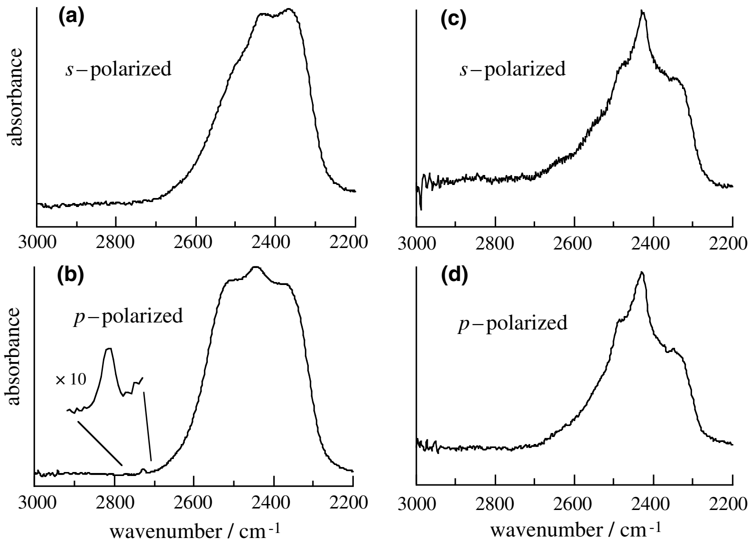

Fig. 3. The 115 K MgO(1 0 0) surface is dosed with D_2O and FTIR spectra are obtained: (a) without annealing, *s* polarization; (b) without annealing, *p* polarization; (c) annealed to 165 K, *s* polarization; (d) annealed to 165 K, *p* polarization. For (a) and (b), surface coverage is ~30 layers. Some water is desorbed during annealing, resulting in ~15 layers for (c) and (d).

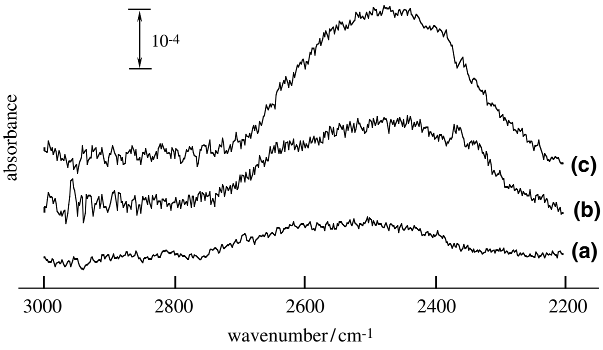

Fig. 4. FTIR spectra of D_2O obtained with a coverage of: (a) a monolayer; (b) 3 layers; (c) 5 layers. The IR beam is unpolarized and $\boldsymbol{k}_{\mathrm{inc}}$ is parallel to the surface normal. Small bumps at ~2350 cm^{-1} are due to small amounts of CO_2 in the beam path. The spectra shown in (a)–(c) were obtained after annealing past the transition temperature.

straightforwardly, as it is due to the very large absorption line widths. Were the same absorption strength contracted into a much smaller line width, the S/N would be very good.

4. Discussion

The manner in which water physisorbs and/or chemisorbs on the MgO(1 0 0) surface is affected by surface morphology, e.g., the type and concentration of defects. MgO(1 0 0) that has been prepared by cleaving in the way described above typically has large terraces, with steps being the most common defect [2]. A number of theoretical calculations have found that water adsorbs molecularly on terraces, with dissociation occurring at steps and edges [3–12]. These calculations were carried out for coverage ranging from a monolayer to many layers.

On the other hand, recent experimental and theoretical work [13,22] suggests that protonated surface oxygen anions and adsorbed hydroxide anions may be present on surfaces that have been exposed to multilayer dosing followed by annealing at higher temperatures. The OH^- and H^+ moieties (with OH^- residing above the magnesium cation and H^+ present on the oxygen anion) are stabilized by surrounding solvent, as well as by their pair-wise interaction. It is noteworthy that they are not formed via multilayer dosing at 100 K. Annealing is required, presumably because of activation energy and/or enhanced mobility. Moreover, adding just a monolayer to the surface at the higher temperatures (i.e., without first adding a multilayer and then desorbing all but the monolayer) does not result in OH^-. It appears that the additional water is instrumental in forming the ion pair, which is not surprising in light of the stabilization brought about through solvation. The roles played by defects are unclear, though it is hard to imagine that they play no role at all. For example, might they create ion pairs that then move to the terrace? In this case, the composition of the observed monolayer could depend on sample and MgO(1 0 0) surface preparation in ways that are not transparent.

In addition to the importance of surface morphology, it is known that low temperature ice has many phases [24–26] and the ice structure depends sensitively on dosing conditions and surface temperature. The O–O distances between neighboring water molecules span a broad range (2.75–2.96 Å) for different forms of the condensed material, e.g., cubic to hexagonal crystals and low to high-density amorphous solids. The Mg–Mg distance of 2.98 Å promotes registry. Namely, because the lattice constant is close to the distances involved in hydrogen bonded water, it is reasonable to assume that a water monolayer, if it exists, is in registry with the surface, and that the water molecules also hydrogen bond with one another.

This registry is confirmed by calculations. Soetens et al. have estimated the O–O distance between neighboring water molecules in the monolayer on MgO(1 0 0) to be about 2.90 Å, whereas in overlayers it is close to the distance of 2.75 Å found in cubic ice. The estimated value of 2.90 Å is in acceptable agreement with the known Mg–Mg distance of 2.98 Å. In our experiments, when many layers were deposited on the 115 K surface, the IR spectra indicated a blend of amorphous and cubic ice. Growth is calibrated by using TPD, and film thickness varies linearly with exposure time for a given temperature and pressure. Absorbances obtained via FTIR also increase linearly with exposure time for unannealed samples.

The transition from amorphous to cubic ice is known to take place at approximately 150 K [24–26], and Fig. 3 shows that this occurs in the films described herein. After dosing at 115 K and before annealing, the films ($\geqslant 10$ layers) display spectral characteristics that are consistent with a combination of cubic ice and amorphous solid. Upon annealing past the transition temperature, however, the cubic ice features become much more prominent. This behavior is consistent with previous work in which this transition has been examined thoroughly [28,29].

The monolayer line shape and intensity are independent of whether this coverage is achieved by using a single layer dose (confirmed by TPD) or, alternatively, by using a large dose followed by annealing to evaporate the overlayers. The MgO surface does not appear to play a significant role in the structure of the ice that forms in the multilayer regime, though it influences profoundly the monolayer.

Referring to Fig. 3, *p*-polarized spectra show a small feature at 2727 cm^{-1} in unannealed films down to coverage of a few layers. This is most likely due to dangling bonds on the surface of the amorphous solid. Annealing results in crystalline ice with no dangling bonds and therefore the disappearance of this feature. Also, this feature is not seen in the monolayer.

The concentration of dangling bonds due to steps and defects on the surface is too small to be detected in this experiment. In contrast, in the experiments of Heidberg et al., [15] narrow peaks (5–10 cm^{-1}) appeared at low coverage and were attributed to defects. The main feature observed in the D_2O v_1/v_3 region in our work maintains its shape from a few layers down to monolayer coverage. It is broad and red-shifted, relative to the corresponding gas phase values, due to hydrogen bonding. We conclude that there is not a significant amount of non-hydrogen-bonded OD, as these species are expected to have narrower line widths than their hydrogen-bonded counterparts. For example, recall the feature at 2727 cm^{-1} assigned to dangling OD.

For a monolayer, the IR peak is displaced to higher frequencies (relative to the multilayer peak) by ~50 cm^{-1} (Fig. 4). This is consistent with higher coverage having more crystalline ice-like structures with shorter hydrogen bond distances, whereas hydrogen bond distances within the monolayer are dictated by registry with the surface [25,26]. The broadness of the infrared absorption spectra compromises sensitivity and makes it difficult to quantify small changes such as shifts that are smaller than the widths, for example, the blue-shift of ~50 cm^{-1}. Polarized radiation shows no difference in the peak shape of the adsorbed monolayer. We conclude that hydrogen bonding continues to have a significant effect on the adsorbates, even at monolayer coverage. The oxygen atoms in the monolayer situate themselves over the magnesium sites, which results in slightly elongated hydrogen bonds. As mentioned earlier, absorption features of the water monolayer are very broad due to hydrogen bonding [26]. This results in low S/N, which cannot be remedied by more diligent effort. Were the absorption features relatively sharp, say a few cm^{-1}, the S/N would be much larger. For example, we find that probe molecules such as CO_2 and N_2O yield high S/N spectra at sub-monolayer coverage [30].

Adsorbate orientation can be obtained from ratios of peak areas recorded with polarized radiation by using the oriented gas model [31]. For the system under consideration (i.e., a 50° angle between $\boldsymbol{k}_{\text{inc}}$ and the surface normal), this yields the curve shown in Fig. 5. Though low S/N and broad peaks preclude the possibility of

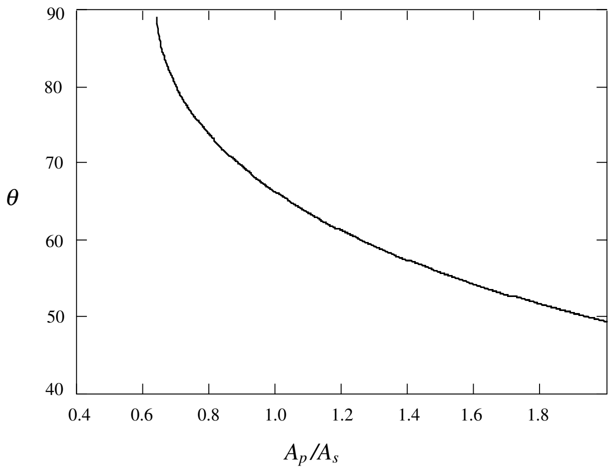

Fig. 5. Angle of transition dipole moment from the surface normal as a function of integrated intensity of polarized light for the MgO(1 0 0)–water system.

obtaining accurate peak areas, absorptions obtained with *s* polarization are consistently larger than those obtained with *p* polarization, suggesting that OD bonds on average lie least 65° relative to the surface normal. This is consistent with the thesis that the monolayer is a hydrogen-bonded network, with OD bonds approximately parallel to the surface. It is also consistent with the broad monolayer spectral feature (Fig. 4), which would be much narrower were there not a hydrogen bonded network. Thus, on average, water lies flat on terraces of the MgO(1 0 0) surface.

The fact that we observe a hydrogen-bonded water network at monolayer coverage does not preclude the possibility that other species are present. For example, it has been pointed out that OH^- might exist in a two-dimensional solvated form paired with surface hydroxide ion [13,22]. If this is the case, hydrogen bonding may broaden the spectral features of these species, confounding their detection. Thus, our data cannot rule out the presence of these ions.

If such species are, in fact, present on terraces, it is likely that they become more important at higher temperatures and arrive there via defect sites, which are more chemically active than terrace sites. The observation that hydroxide is present only after raising the temperature to $\sim$150 K is consistent with such a mechanism [13,22].

In conclusion, the water molecules in the monolayer, for the most part, lie flat on the cleaved MgO(1 0 0) surface and are hydrogen bonded. Spectra in the OD stretch region of hydrogen-bonded water on MgO(1 0 0) are broad, making interpretation difficult. Dangling OD bonds are directed normal to the surface and have a sharp spectral feature at 2727 cm^{-1}. They are present only in unannealed multilayer samples. Whether other species coexist with the water is an open question. An experiment that might be useful in elucidating the structure of thin water films is to cover the water surfaces with small 'probe molecules' that have large IR absorption cross sections and narrow line shapes and record their polarized IR spectra. For example, small probe molecules that can reside within amorphous (but not crystalline) water will enable the degree of porosity to be determined.

Acknowledgment

This work was supported by the US Air Force Office of Scientific Research, under Grant No. F49620-01-1-0071.

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